

Effect of hydrogen on the atomic structure of Pd(001)

S.H. Kim, J. Barthel, H.L. Meyerheim, and J. Kirschner

Max-Planck Institut für Mikrostruktur Physik, Weinbergweg 2, Halle/Salle, Germany

Jikeun Seo

Department of Ophthalmic Optics, Chodang University, Muan 534-701, Korea

J.-S. Kim

Department of physics, Sook-Myung Women's university, Seoul 140-742, Korea

(Dated: February 2, 2008)

The atomic structures of clean and hydrogen-adsorbed Pd(001) are investigated by low energy electron diffraction (LEED) I/V analysis. Clean Pd(001) shows little surface relaxation in sharp contrast to previous reports. Adsorbing 1 monolayer of hydrogen on Pd(001), we observe sizable expansion of the interlayer spacing of the first two surface layers, d_{12} by 4.7% of the corresponding one of bulk Pd. Both experimental observations are in excellent agreement with the predictions of recent *ab initio* calculations. A series of experiments with varying coverages of hydrogen adsorbed on Pd(001), reveals that d_{12} monotonically increases with the increasing coverage. Such an observation strongly supports the contention that the previous observation of expanded d_{12} in clean Pd(001) results from contamination of the surface by residual hydrogen.

PACS numbers:

I. INTRODUCTION

Hydrogen is well known to diffuse and dissolve well in Pd, which has motivated researchers from many different disciplines to investigate Pd-H complex due to its possible application as hydrogen carrier.¹ The adsorption, dissociation and diffusion of hydrogen on single crystalline Pd has been studied as a model system to understand atomistic process of hydrogen incorporation and catalytic behavior of Pd. For Pd(001), numerous experimental works have been performed by employing low energy electron diffraction (LEED)^{2,3}, He ion scattering⁴, work function measurement⁵, thermal desorption spectroscopy (TDS)^{2,6,7}, nuclear reaction analysis (NRA)^{7,8}, electron energy loss spectroscopy (EELS)^{6,9}. Moreover, *ab initio* calculations have been made to study electronic and atomic structures, and chemical properties of Pd(001) upon hydrogen adsorption.^{10,11,12,13} Thereupon, found are many physical and chemical properties of Pd(001) such as dissociation mechanism of H_2 , adsorption sites and adsorption energies of hydrogen, dependence of work function on the coverage of hydrogen, desorption and dissolution kinetics of hydrogen on Pd(001).

The atomic structure of clean and hydrogen-adsorbed Pd(001) is, however, not established yet. Behm *et.al.*² and Jona *et.al.*³ found from their LEED I/V analysis that the interlayer spacing of the first two layers from the surface (d_{12}) expanded by 2.5 %, 3.0 %, respectively, with respect to the corresponding bulk spacing, d_B . Most unreconstructed metal (001) surface, however, show contraction of d_{12} , due to increased bond strength between the two layers resulting from the redistribution of electrons from surface atoms to the first interlayer space.¹⁴ In this regards, the expansion of d_{12} of Pd(001) is an unexpected observation.

As the origin for such an expansion of d_{12} , Jona *et.al.*³ pointed out two possibilities; magnetization of the surface and hydrogen contamination of Pd(001). Magnetization of Pd thin (< 5ML) films grown on Ag(001)¹⁵ and Au(001)¹⁶ was investigated by MOKE, but null magnetization is found. Both self-consistent tight binding calculation¹⁷ and *ab initio* calculation by full potential linearized augmented plane wave method (FLAPW) predicted delicate dependence of magnetization of Pd on the thickness of slab to model Pd(001). (*Note: at the moment we are waiting for the result of Prof. Hong on the effect of magnetization on surface relaxation of Pd(001). He suggested very small, if any, relaxation due to the tiny magnetization of Pd.*) On the other hand, for hydrogen covered Pd(001), expansion of d_{12} is predicted.^{10,11,13} However, no direct experimental investigation has been made yet to examine the correlation between hydrogen coverage and the atomic structure of Pd(001). Such study should be critical to identify the origin of the observed expansion of d_{12} .

The present work is aimed to experimentally clarify the effect of hydrogen coverage on the atomic structure of Pd(001). We carefully prepare Pd(001) with various hydrogen coverages, and investigate their atomic structure by LEED I/V analysis. From that study, we find that there is little expansion of d_{12} for clean Pd(001), while the d_{12} monotonically expands with increasing hydrogen coverage. We also find that the remnant hydrogen in our experimental chamber, although its base pressure is very low, low 10^{-11} mbar, can swiftly contaminate Pd(001) and result in the notable expansion of d_{12} . Combining all the abovementioned observation, we conclude that expansion of d_{12} of clean Pd(001) previously reported by other experimental groups^{2,3}, originates from hydrogen contamination of Pd(001).

II. EXPERIMENTS AND LEED I/V ANALYSIS

A. Experiment

All the experiments were performed in an ultrahigh vacuum chamber with its base pressure low 10^{-11} mbar. The chamber was equipped with rear-view LEED optics and cylindrical mirror analyzer for Auger electron spectroscopy (AES). Pd(001) sample was of "top-hat" shape with its diameter, 8 mm, and thickness, 1 mm. We cleaned the sample by iterating sputtering with 2 KeV Ar^+ and annealing at 950 K for 20 minutes. To remove remnant carbon, we oxidized it by annealing the sample at 650K in an oxygen ambient pressure of 1×10^{-8} mbar, and desorbed it at 950 K, until there was observed no AES peak of carbon. Once the contaminants were removed of the sample, we prepared the sample by sputtering and annealing only for once. From now on, we call this routine sample preparation procedure, *standard* procedure.

For the *standard* procedure, the time required to complete acquisition of I/V spectra was around 2 hours from the start of annealing. During that period, it seemed highly possible that the surface was contaminated by residual hydrogen. Thus, we prepared clean sample in two different ways to ensure cleanliness of Pd(001). The first way was to minimize the time till I/V acquisition; After following the *standard* procedure, we flashed the sample up to 950 K to detach any residual hydrogen and cooled the sample to 150 K within 30 minutes by liquid nitrogen. (Desorption temperatures of surface and subsurface hydrogen, T_D , were known to be lower than 340 K.⁶) Following this *rapid* cleaning process, we could finish the I/V acquisition within 1 hour in the better vacuum condition. The second method was based on the fact that the desorption temperature of hydrogen was around 340 K; We took I/V with the sample at temperatures higher than the desorption temperature.

Hydrogen covered Pd(001) was also investigated as follows; After flashing the sample at 950 K, we cooled it down to 150 K for hydrogen dose, because the hydrogen was known to dissolve into bulk Pd near room temperature.^{6,7} We dosed 6~12 Langmür (L) of hydrogen in an ambient hydrogen pressure, 1×10^{-8} mbar. Since there was little difference in LEED I/V for dosing more than 6 L of hydrogen, we concluded that 6 L of hydrogen was enough to saturate Pd(001). Hydrogen saturated Pd(001) showed $p(1 \times 1)$ LEED pattern with its background intensity about the same as for clean Pd(001) on visual inspection.

B. LEED I/V Analysis

LEED I/V spectra were obtained by a fully automated video-LEED system comprised of a charge coupled device (CCD) camera and a program for image processing. The I/V spectra were always taken with the sample normal

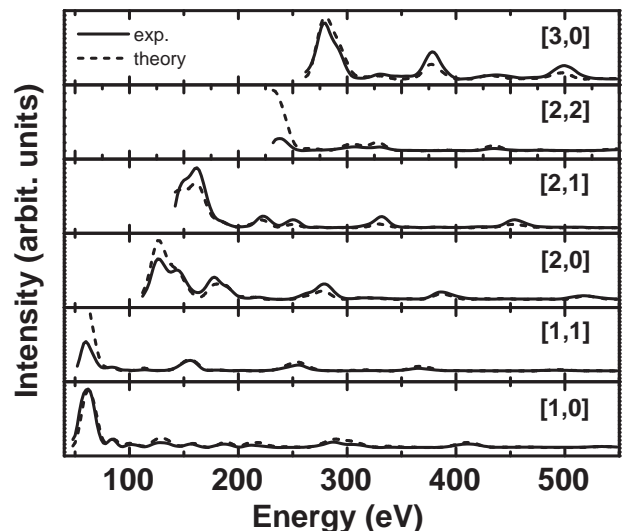


FIG. 1: LEED I/V spectra for *rapidly* cleaned Pd(001). Thick line is experimental curve and the dotted line is theoretical one.

to the electron beam. LEED I/V analysis was made by SATLEED program.¹⁹ Scattering phase shifts were obtained from potentials of Moruzi *et.al.*²⁰ for its angular momentum, l from 0 to 10. Thermal vibration effect was taken into account by Debye-Waller factor with Debye temperatures of H and Pd, 1800 K and 260 K, respectively. We also varied the Debye temperatures as fitting parameters, however, the best-fit atomic structure was not sensitive to them. The quality of I/V fit was judged by the reliability factor of Pendry, R_P , and error limit was set by its variance.²¹ Fitting was made for various model structures, and the best-fit structure was concluded after iterating the fitting till the difference between the input structural parameters and those of the resulting best-fit structure were within 0.001 Å.

III. RESULTS AND DISCUSSION

In Fig. 1, shown are LEED I/V spectra for [1,0], [1,1], [2,0], [2,1], [2,2], [3,0] beams of the *rapidly* cleaned Pd(001). The total energy range of the spectra is 2468 eV. In Table I, summarized are the best-fit structures for three, most conceivable models, given the present experimental condition and the results in literatures. The minimum R-factor is found for clean Pd(001) model and is very small, 0.17, in regards to the large number of beams and extensive energy range of I/V spectra. The theoretical I/V spectra of the best-fit structure in Fig.1 well reproduces most features in the experimental spectra, which purports the present I/V fitting reliable. R_P -factors for the other models, some of which are given in Table I, are outside the variance of the minimum R_P -factor of clean Pd(001), and thus they are excluded for the model of *rapidly* cleaned Pd(001).

TABLE I: Results of LEED I/V analysis for *rapidly* cleaned Pd(001). *Clean*, *Hollow-H*, *Subsurface-H* respectively signifies model structures: clean Pd(001), Pd(001) with 1ML hydrogen in the four-fold hollow site of the surface layer, and Pd(001) with 1 ML of hydrogen in the four-fold hollow site beneath Pd surface layer.

	Model structure	Theory	Experiment
	<i>Clean</i>	LDA	(Jona) ³
$\Delta d_{12}/d_B$	$+0.2 \pm 1.4 \%$	-0.6 %	+3.0 %
$\Delta d_{23}/d_B$	$-0.7 \pm 1.3 \%$	-1.0 %	-1.0 %
R_P -factor	0.170	+0.1 %	0.350
variance	0.0206		

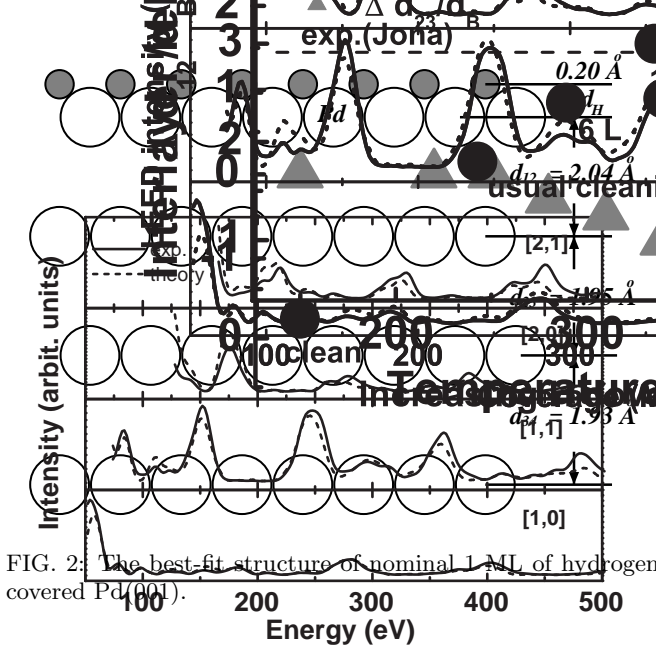


FIG. 2: The best-fit structure of nominal 1 ML of hydrogen covered Pd(001).

The best-fit structure for *rapidly* cleaned Pd(001) shows little surface relaxation (Table I); d_{12} shows a negligible amount of expansion by + 0.2 % of d_B . (From now on, all structural variation is given with respect to d_B .) d_{12} for clean Pd(001) is predicted to contract by less than 1% by recent theoretical works ignoring spin-polarization^{13,22}, which is in good agreement with the present experimental result. Hence, it is likely that the *rapidly* cleaned sample is really clean Pd(001).

The atomic structures of both hydrogen-adsorbed and subsequently hydrogen-desorbed Pd(001) are also investigated by LEED I/V analyses. The I/V spectra are obtained after dosing 6 L of hydrogen on Pd(001) at 150 K and then while gradually warming up the sample beyond T_D . Detailed sample preparation procedure is as described in the experiment section.

In the beginning, the atomic structure of hydrogen-adsorbed Pd(001) at 150 K is investigated by the analyses of LEED I/V spectra for [1,0], [1,1],[2,0],[2,1] beams with their total energy range, 1810 eV. Table II is a summary of the I/V analysis. The best-fit is found for a model where 1 monolayer (ML) of hydrogen is adsorbed on the four-fold hollow site of Pd(001). (Fig. 2) We find that the theoretical I/V spectra for the best-fit structure well reproduce all the experimental features in Fig. 3. The R_P -factor of the best-fit structure is also quite low, 0.1626,

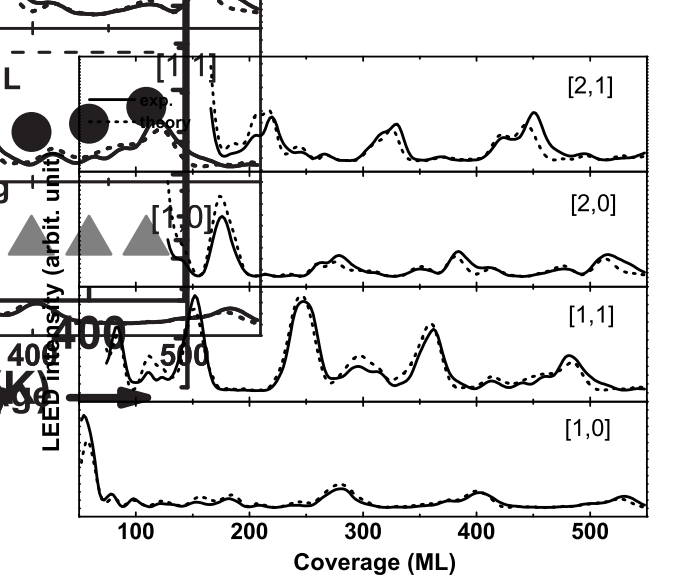


FIG. 3: LEED I/V spectra for the nominal 1ML of hydrogen covered Pd(001). Solid line signifies theoretical result and the dotted one does theoretical spectra for the best-fit structure.

and the other structures result in R_P -factors far beyond the variance of the minimum R_P -factor (Table II), assuring that the best-fit structure represents the atomic structure of the hydrogen-adsorbed Pd(001).

For the best-fit structure (Fig.2 and Table II), the distance between hydrogen and Pd surface layer, d_H , is 0.2 Å. Large error limit of d_H reflects small scattering cross section of hydrogen. d_{12} expands by 4.7 %, and d_{23} and d_{34} show no relaxation. The present observation is in excellent agreement with recent theoretical predictions that four-fold hollow site is the energetically most favored adsorption site of hydrogen till its coverage reaches 1 ML, and d_H is 0.1 ~ 0.25 Å, and d_{12} expands by 4.4 ~ 5.2 %.^{10,11,13} Besides, ion-channeling experiment⁸ predicts d_H to be 0.3 Å. In this experiment, d_H includes Δd_{12} , the variation of d_{12} from d_B . If we also include Δd_{12} to d_H , the resulting value is 0.29 Å, in excellent agreement with the result of ion-channeling experiment, 0.3 Å.

We trace the evolution of its surface structure by LEED I/V analysis while gradually annealing the sample to temperatures higher than T_D , since we expect to obtain clean Pd(001) by desorbing hydrogen from the sample. In Table III, below 340 K, the best-fit model

TABLE II: Results of LEED I/V analyses for H-adsorbed Pd(001) at 150 K. d_H and d_{12} are as defined in Fig. 2. Among others, four most relevant model structures, Pd(001) with hydrogen at fourfold hollow site, *Hollow-H*, *Bridge-H*, *On-top -H*, and *Clean* signify structures where 1 ML of hydrogen is adsorbed respectively on four-fold hollow site, bridge site, and on-top site, and clean Pd(001).

	Model structure				Theory		Experiment ⁸
	<i>Hollow-H</i>	<i>Bridge-H</i>	<i>On-top-H</i>	<i>Clean</i>	LDA ¹¹	GGA ¹³	
d_H	0.20 $^{+0.43}_{-0.22}$ Å	1.21 Å	1.10 Å		0.16 Å(hollow)	0.20 Å	0.3 Å
$\Delta d_{12}/d_b$	+4.7 ± 1.1 %	+5.2 %	+5.8 %	+5.3 %	+5.2 %	+4.4 %	($d_H + \Delta d_{12}$)
$\Delta d_{23}/d_b$	+0.0 ± 0.9 %	-1.0 %	-0.1 %	-0.4 %		+0.2 %	
R-factor	0.1626	0.2720	0.3594	0.2646			
variance	0.0231						

TABLE III: After adsorbing 1 ML of hydrogen on Pd(001) at 150 K, temperature of the sample is gradually raised to 430 K, during which LEED I/V spectra are taken and analyzed. *Hollow-H* signifies a model, 1 ML of hydrogen adsorbed the four-fold hollow site of Pd(001), and *Clean* does clean Pd(001).

Exp. temp.	<i>Hollow-H</i>			<i>Clean</i>	
	d_H	$\Delta d_{12}/d_B$	R_P -factor	$\Delta d_{12}/d_B$	R_P -factor
220 K	0.20 Å	+4.5 %	0.1692	+5.3 %	0.2582
250 K	0.20 Å	+4.4 %	0.1748	+5.2 %	0.2658
280 K	0.21 Å	+4.4 %	0.1826	+5.2 %	0.2733
310 K	0.21 Å	+4.2 %	0.2088	+5.1 %	0.2931
340 K	0.44 Å	+0.5 %	0.2007	+0.9 %	0.2004
400 K	0.33 Å	+0.6 %	0.1956	+0.6 %	0.1873
430 K	0.61 Å	+0.7 %	0.2043	+0.8 %	0.1899

is Pd(001) with 1 ML of hydrogen adsorbed on four-fold hollow site. Further, d_{12} and d_{23} are maintained around the same value as that at 150 K. If the sample temperature (T_S) is raised higher than T_D , the best-fit model switches from hydrogen-adsorbed Pd(001) to clean Pd(001) (Table III), and both d_{12} and d_{23} simultaneously show such abrupt contraction as demonstrated in Fig. 4. Although the R_P -factors of both structures are within the variance of the minimum R-factor, such an observation of the change of the best-fit structure is consistent with the observation of hydrogen desorption at 340 K.^{6,7} Δd_{12} for T_S higher than T_D , is +0.6~0.9 %, which is in good agreement with that found for the *rapidly* cleaned Pd(001). From the agreement of the atomic structures of the two differently prepared clean Pd(001), we conclude that clean Pd(001) must have almost the bulk-terminated structure, while hydrogen-adsorbed Pd(001) shows notable expansion of the d_{12} .

Although clean Pd(001) found in the present experiment show little surface relaxation, previous experiments report the expansion of d_{12} by 2.5 % to 3 %.^{2,3} The observation of the expansion of d_{12} upon hydrogen adsorption suggests that the previous experiments were performed with hydrogen-contaminated Pd(001). For the direct examination of such possibility, we perform the sample preparation and the I/V acquisition in the *standard* way without making extra-efforts such as flash cleaning and

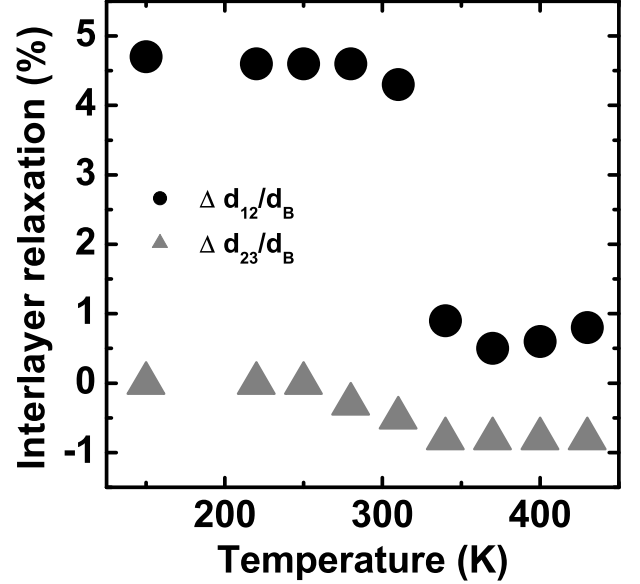


FIG. 4: Dependence of Δd_{12} and Δd_{23} on sample temperature.

rapid cooling as made in the *rapid* cleaning procedure. This experiment may correspond to a replication of previous experiments.

In Table IV, given is a summary of I/V analyses for Pd(001) cleaned via the *standard* procedure. The most notable result is that d_{12} increases by 1.8 % (Also, see Fig. 5), which clearly contrasts to the almost bulk-terminated structure of clean Pd(001). d_{12} in the present experiment, however, expands less than in previous reports, 2.5 % to 3 %.^{2,3} The reason why different amount of expansion of d_{12} is observed experiment by experiment is supposed to be different degree of hydrogen contamination resulting from different base pressure and duration of experiment. To directly examine this conjecture, we dose varying amounts of hydrogen on Pd(001) at *room temperature*, and investigate the dependence of the atomic structure on hydrogen dosage by LEED I/V analysis.

In Table IV, given are the best-fit structures of Pd(001) 1) prepared via *standard* cleaning and 2) dosed respectively by 6 and 12 L of hydrogen at room temperature.

TABLE IV: LEED I/V analyses are made for Pd(001) cleaned via *standard* procedure, and for 6 (6L-H) and 12 L (12L-H) of hydrogen-dosed Pd(001). Respective I/V is fit, assuming clean Pd(001) to compare with previous results.

	$\Delta d_{12}/d_B$	$\Delta d_{23}/d_B$	R_P -factor
<i>standard</i>	+1.8 %	-0.7 %	0.1944
6L - H	+2.4 %	-0.7 %	0.2095
12L - H	+3.0 %	-1.0 %	0.2235

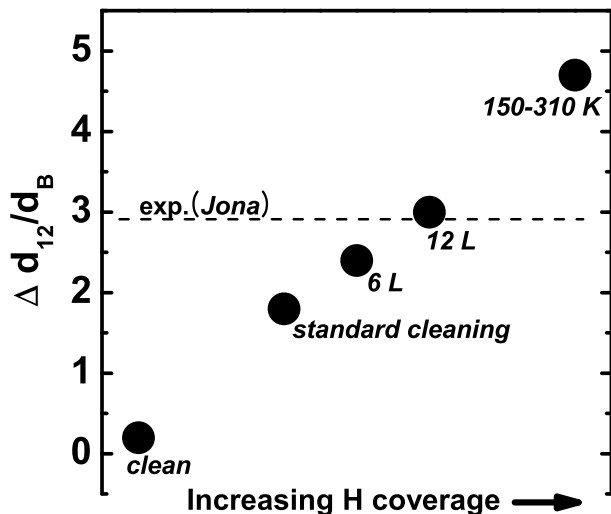


FIG. 5: $\Delta d_{12}/d_B$ is presented for increasing hydrogen coverage. The x-axis just indicates the direction of increasing hydrogen coverage, but is not in proportion. *clean* signifies clean Pd(001) prepared by *rapid* cleaning (Table I). *150-310 K* refers to mean Δd_{12} of 1 ML of hydrogen-covered surfaces from 150 K to 310 K. (Table III) *Standard cleaning* indicates Pd(001) cleaned via *standard* procedure, and 6L and 12L do Pd(001) dosed with the respective amount of hydrogen at room temperature. *Jona* refers to Jona et. al.'s experiment.³

When 6 L of hydrogen is dosed, d_{12} expands by 2.4 %, while it does by 3.0 % with increased dosage of 12 L. In regards to the fact that d_{12} expands by 4.7 % for hydrogen saturated surface at 150 K, we find monotonic increase of Δd_{12} with increasing amount of hydrogen coverage. (Fig. 5) From the above account, the reason why the amount of expansion of d_{12} varies experiment by experiment is evidently the different degree of hydrogen contamination due to different sample cleaning procedure and/or experimental environment. In short, the previous experimental results of expanded d_{12} of clean Pd(001) is attributed to the contamination by residual hydrogen.

IV. SUMMARY

We prepare clean Pd(001) in two different ways, *rapid* cleaning and hydrogen desorption, and consistently find by LEED I/V analysis that the atomic structure of clean Pd(001) is similar to bulk-terminated Pd(001). (Fig. 1 and 4) On the other hand, hydrogen covered surface shows monotonic increase of d_{12} with increasing hydrogen coverage. (Fig. 5) The present, systematic study on the effect of hydrogen on the atomic structure of Pd(001) firmly conclude that the previously reported expansion of interlayer spacing of Pd(001) originates from hydrogen contamination of the sample.

Acknowledgments

-
- ¹ W. M. Mueller, J. P. Blackledge, and G. G. Libowitz (Eds), *Metal Hydrides*, (Academic Press, New York, 1986).
 - ² R. J. Behm, K. Christman, G. Ertl, M. A. Van Hove, P. A. Thiel, and W. H. Weinberg, *Surf. Sci.* **88**, L59 (1979).
 - ³ J. Quinn, Y. S. Li, D. Tian, H. Li, and F. Jona, *Phys. Rev. B* **42**, 11348 (1990).
 - ⁴ K. H. Rieder and W. Stocker, *Surf. Sci.* **149**, 139 (1984).
 - ⁵ R. J. Behm, K. Christman, and G. Ertl, *Surf. Sci.* **99**, 320 (1980).
 - ⁶ H. Okuyama, W. Siga, T. Takagi, M. Nishijima, and T. Aruga, *Surf. Sci.* **401** 344 (1998).
 - ⁷ M. Wilde, M. Matsumoto, K. Fukutani, and T. Aruga, *Surf. Sci.* **482-485**, 346 (2001).
 - ⁸ F. Besenbacher, I. Stensgaard, and K. Mortensen, *Surf. Sci.* **191**, 288 (1987).
 - ⁹ C. Nyberg and C. G. Tengstal, *Phys. Rev. Lett.* **50** 1680 (1983).
 - ¹⁰ D. Tománek, Z. Sun, S. G. Louie, *Phys. Rev. B* **43**, 4699 (1991).
 - ¹¹ S. Wilke, D. Hennig, and R. Löber, *Phys. Rev. B* **50**, 2548 (1994).
 - ¹² S. Wilke and M. Scheffler, *Phys. Rev. B* **53**, 4926 (1996).
 - ¹³ A. Eichler, J. Hafner, and G. Kresse, *J. Phys. : Condens. Matter* **8**, 7659 (1996).
 - ¹⁴ P. J. Feibelman, *Surf. Sci.* **360**, 297 (1996).
 - ¹⁵ R.L. Fink, C.A. Ballentine, J.L. Erskine, and J. Araya-Pochet, *Phys. Rev. B* **41**, 10175 (1990).
 - ¹⁶ C. Liu and S. D. Bader, *Phys. Rev. B* **44**, R12062 (1991).
 - ¹⁷ H. Dreyssé, A. Mokrani, S. Bouarab, and C. Demangeat, *Surf. Sci.* **251-252**, 41 (1991).
 - ¹⁸ S. C. Hong (unpublished).
 - ¹⁹ P. J. Rous, J. B. Pendry, D. K. Saldin, K. Heinz, K. Müller, and N. Bickel, *Phys. Rev. Lett.* **57**, 2951 (1986); A. Wandler, M.A. van Hove, and G.A. Somorjai, *Phys. Rev. Lett.* **67**, 626 (1991).
 - ²⁰ V. L. Moruzzi, J. F. Janak and A. R. Williams, *Calculations of Electronics Properties of Metals*, Pergamon, New York (1978).

²¹ J. B. Pendry, J. Phys. C **13**, 937 (1980).

²² M. Methfessel, D. Henig, and M. Scheffler, Phys. Rev. B

46, 4816 (1992).